

Perlite Waste As A Precursor For Geopolymer Formation

E. R. Vance¹, D. S. Perera¹, P. Imperia¹, D. J. Cassidy¹, J. Davis¹ and J. T. Gourley²

¹*Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Menai, NSW 2234, Australia*

²*Geopolymer Alliance, Curtin University, Bentley, WA 6012, Australia*

Email: erv@ansto.gov.au

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Abstract

Waste perlite can be reacted with alkaline solutions to form crystalline zeolite 4A and other minor crystalline phases. The fine majority fraction of the waste was fairly reactive and the coarse fraction largely acted as a filler. This geopolymer had poor compressive strength, but when perlite was used in conjunction with flyash, geopolymers of acceptable mechanical properties could be made. Perlite shows significant reaction with 10 Mol/L NaOH solution at ~ 70°C, with hydroxysodalite appearing as a reaction product.

Keywords: geopolymers, perlite residues, FTIR, zeolite, compressive strength

INTRODUCTION

Perlite is derived from volcanic sources and after size reduction and heating to render it porous via the escape of water, it is used as a water absorbent in agricultural applications. Waste perlite arises in the manufacturing process as unwanted particle size ranges or material that has not become adequately porous. Perlite is X-ray amorphous and has the basic composition of around 80 wt% SiO₂, 15 wt% Al₂O₃, and a few wt% of alkali. As a candidate reactive waste aluminosilicate we have explored the possible use of this material as a useful constituent of geopolymers for construction material or immobilisation of hazardous/radioactive waste. Work has been carried out on the addition of waste perlite to Portland cement, but the perlite imparted only a minor contribution to the strength [1].

In the present work the targeted materials were geopolymers [2, 3] normally derived from the action of strong alkaline silicate solutions on reactive aluminosilicate precursors, using minimum water contents, followed by curing in sealed systems for a day or so at 40-80°C [2]. While such materials are similar to ordinary Portland cement, geopolymers have several potential advantages over the former, in relation to only ~ one-sixth of greenhouse gas emissions per unit mass of cement during production, as well as better acid and fire resistance. Geopolymers are increasingly considered as a low energy consuming “green” material.

METHODS AND PROCEDURES

We had access to “fine” (100% < 500 µm) and “coarse” (12% > 500 µm) material. The particle

size distributions are shown in Fig. 1. Tap densities were around 0.2 and 0.8 g.cm⁻³ respectively. Differential thermal and thermogravimetric analysis (DTA/TGA) results were obtained using a Setaram instrument and a heating rate of 10°C/min. with a ~ 90 mg sample pressed into a pellet and contained in a Pt sample cup, with a reference cup containing alumina powder.

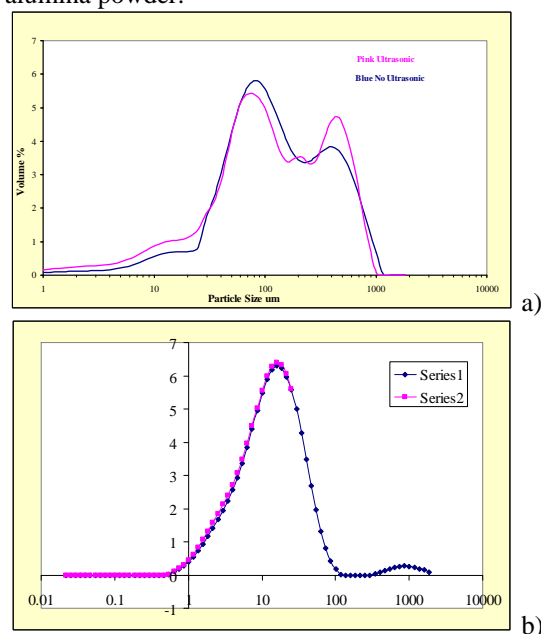


Fig. 1 Perlite particle size distributions (a) coarse and (b) fine.

Fabrication was undertaken with the aim of making geopolymers with Na/Al and Si/Al molar ratios of around 1 and 2 respectively to maximise strength

and leach resistance in water [4-6]. Because of the low Al content of the perlite, water-soluble Na aluminate was added as an extra source of Al. Also, because of the high SiO₂ content of the perlite, NaOH solution was added rather than an alkali silicate solution. Perlite geopolymers having a nominal molar composition of Si/Al = 1.93 and Na/Al = 1.04 were made by mixing perlite (in the ratio of 30:70 wt% coarse to fine). This value was somewhat arbitrarily chosen as the waste material consists of mainly (~ 90%) fines, but it was of interest to see if the coarse material played a role.

Table 1: Batch compositions of geopolymers (wt%)

Sample	Perlite-based	Fly ash-containing
Coarse perlite	9.6	8.5
Fine perlite	22.5	19.8
Fly ash	-	41.1
NaOH	3.3	2.9
NaAlO ₂	12.4	10.9
DIW	52.2	16.8

For the perlite-based samples, NaOH and NaAlO₂ and minimum deionised water (DIW) were used to obtain a workable mix via hand mixing (see Table 1). After casting, the slurry was cured at 60°C for 4 days. Because the cast material was very porous, exhibited bleed water and relatively fragile, even after some compositional adjustments (see below) a further geopolymer was made by adding fly ash to the abovementioned solids. The Gladstone (Qld., Australia) power station fly ash composition (wt%) was: SiO₂ (54.4), Al₂O₃ (24.8), Fe₂O₃ (16.1), CaO (1.8), Na₂O (1.3), H₂O (1.6). This material had far less water demand than the flyash-free material (Table 1).

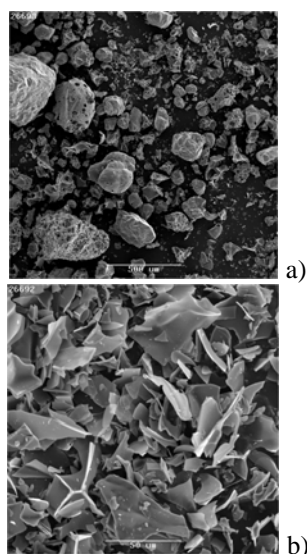


Fig. 2 Secondary SEM images of (a) coarse and (b) fine perlite.

X-ray diffractometry (XRD) was carried out on a Siemens D500 instrument, using Co K α radiation and a graphite monochromator. Scanning electron microscopy (SEM) was performed with a JEOL JSM-6400 instrument at 15 keV, fitted with a Noran Instruments Voyager Series IV X-ray microanalysis system. The geopolymers for SEM examination were polished to a 1 μ m diamond surface finish and coated with a thin carbon layer.

BET measurements were carried out with a Micromeritics ASAP2400 instrument. Samples were conditioned at 100°C in a vacuum for 16 h before measurement.

The diffuse reflectance Fourier transformed infrared (DRIFT-IR) spectroscopy measurements were performed with a Nicolet Nexus 8700 spectrometer in the spectral region 500-4000 cm⁻¹ with a diffuse reflectance accessory of Thermo installed. 10% weight of sample was mixed with spectroscopic grade KBr and reduced to a fine powder in an agate mortar. Data were analysed using the Kubelka-Munk transformation, with a finely ground KBr sample used to determine the background level. Despite the difficulty of reaching quantitative conclusions from DRIFT measurements, qualitative analysis of the spectra allows the essential nature of the absorbing species to be determined with good accuracy.

Cold crushing strength (CCS) specimens, 25 mm diameter and 40 mm high, were cast for each batch. Each specimen was ground flat (flat surfaces) and parallel using silicon carbide paper prior to testing. The CCS tests were conducted at ambient in a servo-electric universal mechanical testing machine (Instron 8562) with a 100 kN load cell. The specimens were tested at a cross-head speed of 5 μ m/s and a minimum of 5 specimens for each composition were tested.

The intrinsic reactivity of the waste perlite with fairly strong (10 Mol/L) caustic soda solution contained in covered plastic beakers on hotplates and using magnetic stirring was studied, using methodology which was fairly similar to that of Chen-Tan et al. [7]. 1g samples of fine perlite were reacted with 25 mL of the NaOH solution for several hours at temperatures between 25 and 75°C using magnetic stirrers in sealed containers. After reaction, the residual solids were washed by adding to several hundred mL of DIW and then filtered. The residues were washed again with 200 ml of DIW, and then dried overnight at 80°C, and weighed.

RESULTS and DISCUSSION

Perlite characterisation

X-ray fluorescence analysis of perlite heated 3 h in air at 1000°C gave the following results (elemental wt%; rest oxygen): Na (1.9); Mg (0.3); Al (6.9); Si (33.6); S (1.1); K (5.1); Ca (0.9); Fe (1.0). Elements having abundances of < 0.1% were ignored. The SEM images of coarse and fine perlite as loose powders are shown in Fig. 2.

The DTA/TGA results for perlite heated in air are shown in Fig. 3(a). The most likely source of the exothermic behaviour is the combustion of carbonaceous material and this was confirmed when another experiment was run in an argon atmosphere (Fig. 3(b)). Weight losses on heating and BET surface area data are shown in Table 2. The small weight loss is ascribed to the desorption of gas species from the surface of the perlite powder, noting that there was virtually no sign of water or hydroxyl ions from IR spectroscopy (see Fig. 4 below) for samples heated at 300 and 1000°C, bearing in mind of course that the waste perlite had already been heated to temperatures of around 850°C in the manufacturing process, before size reduction. Because of the non-combustion of the carbonaceous material, the fractional weight loss was also lower when heating was carried out in argon.

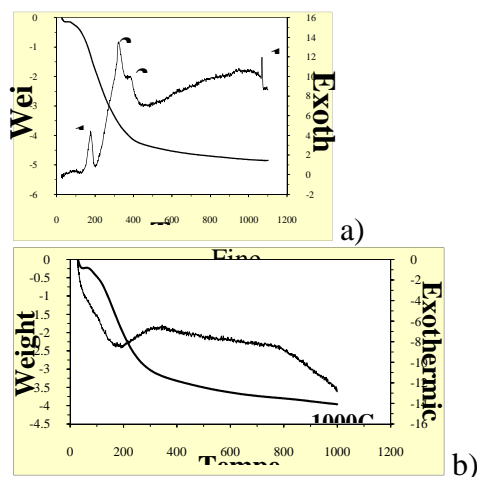


Fig. 3 DTA/TGA results for waste perlite heated in (a) air and (b) Ar.

Fig. 4 shows the FTIR spectra of the perlite as prepared and after heating at 300 °C and 1000 °C (middle and top curves, respectively). The spectra were normalised at their absorption maxima and a vertical offset added for clarity. The inset shows an enlargement of the spectra from the region between 4000 and 1000 cm^{-1} . The region 500 cm^{-1} to 1500 cm^{-1} is characterised by the presence of the main absorption structures, an intense band at about 1030 cm^{-1} with a second intense peak at about 1135 cm^{-1} . These two peaks, labelled d and e, are respectively attributed to Si-O-Si and Si-O-R asymmetric

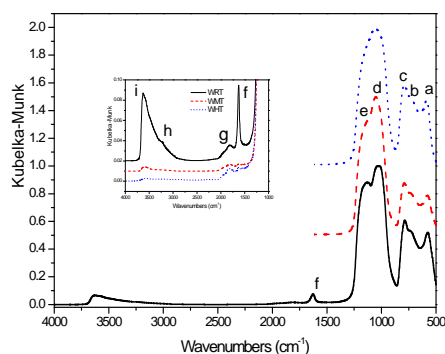
stretching where R can be Al or Si. A further group of three peaks of medium intensity is present at lower wavenumbers: c (787 cm^{-1}), b (730 cm^{-1}) and a (575 cm^{-1}). This group remains unaltered in shape, position and intensity with the annealing. Peak c is attributed to symmetric stretching of Si-O-Si, b to bending of Si-O-Al, and a to symmetric stretching of Si-O-R.

The evolution of the peak e with increasing annealing temperature is an intriguing feature and could be attributed to a rearrangement of the Si-O-Al as the interstitial water is progressively evolved, with the annealing producing a better ordering of the chains.

Table 2: Weight loss on heating and BET surface area data on coarse and fine perlite residues.

Sample	Weight loss, %	Surface area (m^2/g)
Fine perlite	1.73 (conditioning)	2.6
Fine perlite, 1h 750°C	0.59	2.6
Fine perlite, 1h 1000°C	0.32	1.2
Coarse perlite	0.28 (conditioning)	0.8
Coarse perlite, 1h 900°C	Not measured	0.46

A different explanation could be responsible for changes connected with a diminishing fraction of amorphous silica present as the annealing temperature is increased. The main fused silica IR peak is expected at 1126 cm^{-1} [8]. If peaks d and e of the unannealed and annealed at 1000 °C samples are compared, the two peaks perfectly overlap at the higher wavenumber edge, while on the lower wavenumber side changes of the relative intensity of the peaks inside the absorption band are evident, with a shoulder appearing near to peak d. It is on this side of the band that the main changes take place with annealing. This observation, combined with the low annealing temperature, denies the hypothesis of a diminishing fraction of amorphous silica with increasing annealing temperature.



WRT = ambient

WMT = heated at 300oC

WHT = heated at 1000oC

Fig. 4 Infrared spectra of waste perlite-unheated (black line); after heating at 300 oC (dashed line) and 1000 oC (dotted line).

Al-OH and Si-OH bending and stretching bands, expected in the range 955- 830 cm^{-1} , are not observed. A decrease of the shoulder at 915 cm^{-1} with the increase of the annealing temperature should be expected with the formation of Al-OH and Si-OH groups [8]. This confirms an increase of the ordering with the annealing temperature, imparting strength to the Si-O in-plane vibrations [9].

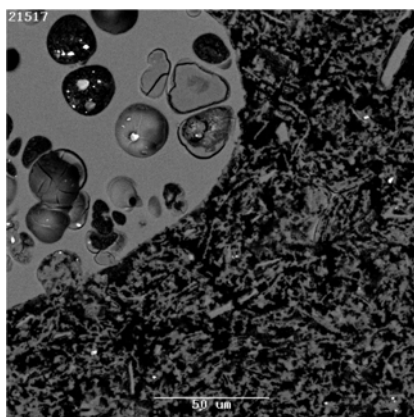


Fig. 5 Backscattered SEM image of the perlite + NaAlO_2 + NaOH geopolymer showing unreacted coarse and fine perlite plus void space.

The unheated (by us in the present work) sample contains some lattice water. The broad structure around 3650-3000 cm^{-1} (peaks i and h) can be attributed to molecular water and asymmetric and symmetric H-O-H stretching vibrations. The intensity of this vanishes once the sample has been heated. The presence of a sharp peak at 1627 cm^{-1} , typical for lattice or interstitial water and not present in the Si-OH or Al-OH complexes, confirms the lattice-interstitial nature of the observed water.

The composite peak g is not affected by the annealing and could be tentatively attributed to Si-H and Al-H stretching bands.

Geopolymers

First attempts at making geopolymers showed that the perlite had a high water demand so it was not surprising that setting by curing by conventional methods in sealed systems at $\sim 60^\circ\text{C}$ led to soft materials with several percent of excess water. Although this could be removed by evaporation, the products were quite soft and could be readily deformed by hand. However by further drying up to 4 days a material resulted that could be handled without breaking. Some reaction with the caustic soda was evidenced as crystalline zeolite A formed together with minor crystalline phases. XRD analysis showed mainly the presence of crystalline 4A zeolite, plus weak lines at d-spacings of 0.63, 0.48, 0.39 nm as well as a broad peak between 20 and 40 deg. in 2θ . The strongest of the crystalline peaks however was only a factor of 2-3 times greater than the height of the broad peak. While a geopolymeric phase would give rise to such a broad peak, the amorphous nature of the original perlite would also yield a similar result. The formation of the zeolite phase is characteristic of the nominally reacted material having a Si/Al molar ratio of around 1[2,3], rather than the value of 2 expected if all the perlite took part in the reaction. Further mixtures using the same solids ratios were made up using $\sim 20\%$ less water with vigorous hand mixing and bleed water was minimal, though the materials still lacked significant strength. XRD showed that the crystalline Na aluminosilicate phases were different than zeolite 4A, with the main one corresponding to the JCPDS 48-731 phase.

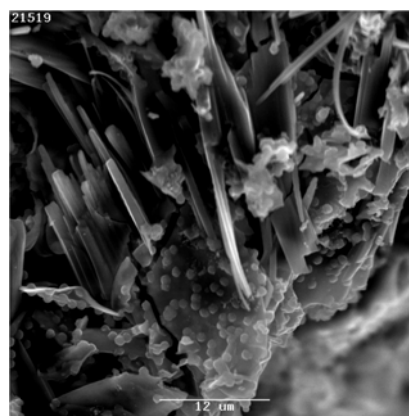


Fig. 6 Backscattered SEM image of perlite + NaOH geopolymer showing unreacted fine perlite flakes plus Na aluminosilicate crystals in void space.

Backscattered SEM images of the perlite-only material are shown in Fig. 5. The solid phase was clearly unreacted coarse perlite plus fine perlite surrounded by a Na-rich phase on the rims of the pores, probably derived from the original NaOH solution forming an alkaline pore water which had subsequently dried, noting that the strength of the NaOH solution was only ~ 1.6 Mol/L (see Table 1). No clear evidence of the zeolite evidenced in XRD was visible in SEM so it was assumed that the zeolite grain size was very fine.

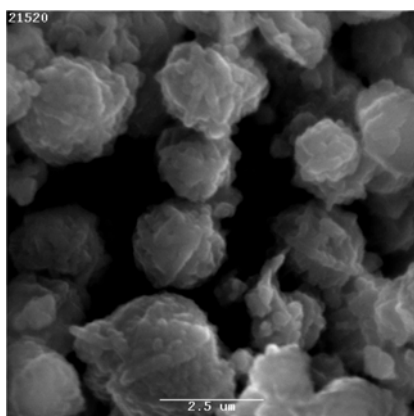


Fig. 7 SEM of sodalite crystal aggregates formed by reacting fine perlite with 10 Mol/L NaOH solution for 20 h at 70°C.

Samples were also made using stronger (~ 5 Mol/L) alkali solution to induce more reaction, and without the sodium aluminate to encourage the formation of a reacted material which did not contain zeolite by increasing the Si/Al molar ratio [1]. However such materials were still basically lacking in strength, although somewhat stronger than the abovementioned material. Na aluminosilicate phases were again observed by XRD, with the main one corresponding to JCPDS 44-103, and SEM showed the presence of these crystalline alteration products (see Fig. 6). The porosity of both materials was quite high ($\sim 30\%$) from SEM examination.

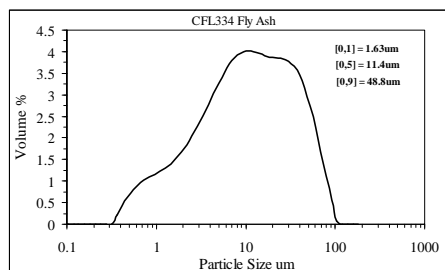


Fig. 8 Particle size distribution of Gladstone flyash.

Reactivity of the fine perlite with 10 Mol/L NaOH solution

The intrinsic reactivity of the fine perlite in the NaOH solution was $< 5\%$ after 2 and 20 h exposure at 25°C in terms of measurable perlite weight loss. No crystalline alteration products were detected by

XRD. However reaction at 55°C produced weight losses of $\sim 20\%$ after 2 h and $\sim 80\%$ after 20h, while at 75°C, weight losses were $\sim 80\%$ after 2 and 20 h, these temperatures spanning the curing temperatures used for geopolymer fabrication. XRD showed the formation of a crystalline sodalite-type alteration phase in these materials and SEM of the material is shown in Fig. 7, showing that the sodalite consisted of micron-sized fairly equiaxed crystals, in keeping with the cubic nature of the basic sodalite structure. Although the absence of exactly flat surfaces precluded quantitative EDX analysis (not to mention alkali migration), it was clear that the sodalite stoichiometry was approximately as expected (roughly Na/Al ~ 1 and Al/Si ~ 1 on a molar basis).

Addition of flyash

A particle size distribution for the Gladstone flyash is shown in Fig. 8. A backscattered SEM image of perlite/fly ash material is shown in Fig. 9. Unreacted coarse perlite can be seen along with iron-rich phase and mullite. Quartz, hematite and mullite were present in the original fly ash. In SEM/XRD, an amorphous phase was observed, of approximate composition to that observed in the initial perlite-only geopolymer sample, together with crystalline quartz, mullite, hematite and 4A zeolite.

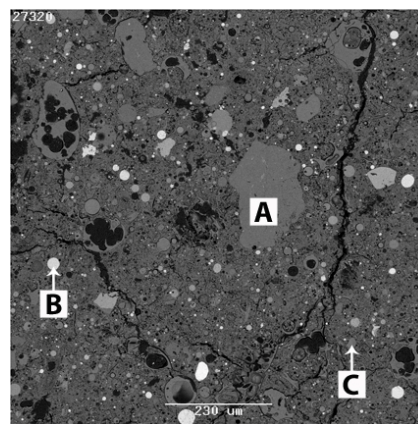


Fig. 9 Backscattered SEM image of perlite/flyash geopolymer. Phases seen are unreacted perlite (A), Fe-rich phase (B) and mullite (C).

The compressive strength of the perlite/flyash geopolymer was measured at 37 MPa, quite a satisfactory value for construction material and more than adequate for waste immobilisation media. The much lower water demand of this material relative to the flyash-free material (Table 1) is worthy of comment.

When flyash is added to the binder mixture, the fine, predominantly rounded particles fill up much of the void space associated with the low tap density of the fine perlite particles, increasing the tap density considerably.

This in turn reduces the fluid demand required to achieve a workable mixture; Table 1 shows the fluid demand dropped from 68 wt % to ~ 31%.

As geopolymer compressive strength is inversely proportional to water content, this effect, along with the likely greater reactivity of the flyash is clearly responsible for the compressive strength rise from near zero to 37 MPa.

CONCLUSION

The fine fraction of the perlite waste can act as a fairly reactive aluminosilicate constituent with strong alkali solution in geopolymer formation. While the minor coarse component does not appear to contribute significant mechanical strength it can act as a filler. The perlite waste as a whole could be used in conjunction with fly ash or other waste aluminosilicates such as ground blast furnace slag for construction material and immobilisation of hazardous/toxic waste.

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